Mass Cascades and Anomalous Scaling in Cluster-Cluster Aggregation

Aerosols, emulsions and gels are a class of binary mixtures in which particles of one phase are dispersed in a continuous matrix of another. Everyday examples include suspensions of particulates in air which form smog, emulsions of essential coffee oils in water creating expresso or cheese - gels of water and oils dispersed in a solid milk-protein matrix. These mixtures are important in many branches of science and engineering from atmospheric science to organic chemistry to astrophysics. They exhibit a variety of interesting physical phenomena. These include flocculation (an instability of an emulsion which leads to the dispersed phase forming clusters and eventually separating out), gelation (the emergence of a macroscopically connected cluster of the dispersed phase of an emulsion, usually causing substantial changes in the material properties of the mixture) and phase separation or creaming (spontaneous spatial separation of the two phases). In studying such phenomena, it is important to take into account transport of the dispersed particles within the continuous phase and the interactions between them.

To create a simple stochastic model of such phenomena, imagine a cloud of initially monodisperse (uniformly sized) particles which move by diffusion with some diffusion constant, D. When two particles of mass m_1 and m_2 happen to meet, they stick together with some with some probability, given by a rate, $\lambda(m_1, m_2)$, to form a new particle of mass $m_1 + m_2$. Obviously the aggregation of particles means that an initially monodisperse mixture will not remain so. At later times, the mixture is characterised by a non-trivial mass distribution, $N_m(t)$, which gives the average density of particles of mass m. It evolves as a function of time. One can imagine intuitively that, if light particles are injected into the mixture at a constant rate, the system may approach a statistically steady state where the addition of light particles is balanced by the creation of heavier particles by aggregation. More careful analysis shows that this is indeed the case. Such a model of cluster aggregation, in the presence of a source of light particles, produces a stationary state which is not unlike the stationary state of a turbulent system. It exhibits a mass cascade which transports mass from small clusters to large and is characterised by a constant flux of mass through all cluster sizes. In practice, to attain a true stationary state, one must add a sink which removes clusters larger than some large mass cut-off. The small mass physics is, however, insensitive to what ultimately happens to the largest clusters.

A mean field theory determining $N_m(t)$ was derived by Smoluchowski in 1917. In Smoluchowski's theory, $N_m(t)$ is determined by the kinetic equation:

$$\partial_t N_m(t) = \int_0^m dm_1 \lambda(m_1, m-m_1) N_{m_1}(t) N_{m-m_1}(t) \quad (1)$$
$$-2N_m(t) \int_0^\infty dm_1 \lambda(m, m_1) N_{m_1}(t) + J\,\delta_{m,1},$$

where the integral terms describe aggregation and the last term injects particles of mass 1 at a rate J. This equation goes some way to describing the physics of aggregation. For $J = 0$, it has decaying solutions describing the generation of heavier clusters by aggregation. For finite J, it produces a stationary solution at large times describing a mass cascade. It even provides an elemenary model of the gelation transition for appropriate choice of the kernel, $\lambda(m_1, m_2)$. It's main weakness lies in the fact that, since it is a mean field theory, it ignores correlations between particles. Like in many systems in statistical physics, in low enough dimensions, such correlations become strong and the Smoluchowski theory fails. The critical dimension in this case is two. Understanding the statistics of the model in dimensions less than or equal to two is a non-trivial problem, which we now address.

From now on, we consider the simplest possible case : the aggregation kernel is a constant, independent of mass: $\lambda(m_1, m_2) = \lambda$. In this case, the mean field solution for the stationary mass density is

$$N_m = c_1 \sqrt{\frac{J}{\lambda}}\, m^{-\frac{3}{2}}. \quad (2)$$

This is correct for $d > 2$. For $d \leq 2$ we expect it to be modified by diffusive fluctuations. Using Doi's method, a fairly standard approach for deriving continuum descriptions of stochastic particle systems, it is possible to convert the master equation for the model into a quantum field theory which can then be analysed using powerful methods of statistical field

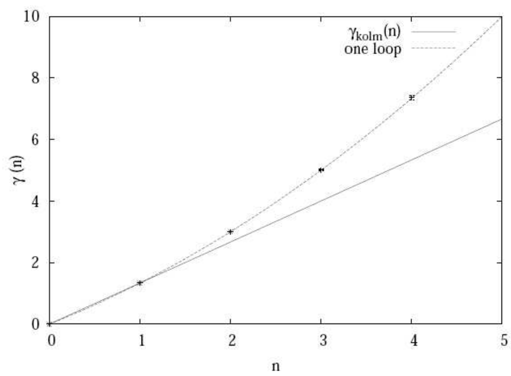

Figure 1: Scaling exponents, γ_n, as a function of n from Monte Carlo simulations.

theory. The coupling constant for the theory is the aggregation rate, λ. When one performs an expansion of the average particle density in powers of λ one finds that the first correction to the mean field answer is divergent for $d \leq 2$ necessitating a resummation of the expansion. This resummation can be achieved using dynamical renormalisation group, or, due to a simple structure inherited from the fact that the kernel is a constant, may be carried out explicitly. It turns out that all divergences in the expansion for the average density are eliminated by renormalisation of λ resulting in the following density for $d < 2$:

$$N_m = c_2 \left(\frac{J}{D}\right) m^{-\frac{2d+2}{d+2}}. \tag{3}$$

We now consider higher order correlation functions of the density. It turns out that a natural object to study is $C_n(m_1 \ldots m_n)$ which is the probability of finding n particles, $m_1 \ldots m_n$, within a small volume of space. In particular, we would like to know how these objects scale as the masses become large, $C_n(m) \sim m^{-\gamma_n}$, as characterised by a set of exponents, γ_n. If the stationary distribution is self-similar then the n-point correlation function should be given by the n^{th} power of the density so that $\gamma_n = \frac{2d+2}{d+2} n$. Otherwise, the particle distribution exhibits a multifractal character. We immediately find that multifractality is unavoidable in this model. By an exact calculation, which is very closely related to the argument which yields the $4/5$-law for hydrodynamic turbulence, one can show that $C_2(m_1, m_2) \sim m^{-3}$ in all dimensions. This is the mean-field answer. Physically, it tells us that the average mass flux is insensitive to fluctuations.

The C_n for $n \geq 3$ cannot be calculated exactly. However they can be calculated pertubatively. For $d \leq 2$ there are additional divergences in the perturbative expansion of the C_n about their mean field values. These come from non-factorization of certain composite operators in the theory. Unlike the divergences associated with coupling constant renormalisation, these cannot be resummed explicitly making the renormalisation group approach essential. The γ_n are thus obtained as an ε-expansion where $\varepsilon = 2 - d$:

$$\gamma_n = \frac{2d+2}{d+2} n + \frac{1}{2}\frac{n(n-1)\varepsilon}{d+2} + \mathrm{o}(\varepsilon^2). \tag{4}$$

The nonlinear scaling with n confirms the multifractality of the mass distribution. This expression with $\varepsilon = 1$ is compared with Monte Carlo simulations done in $d = 1$ in Fig. 1. The agreement is surprisingly good. Given the approximations involved, one is tempted to conjecture that the lowest order ε-expansion is actually exact.

Physically, these multifractal exponents have the following meaning. Given that the γ_n are greater than the (linear) self-similar exponents, the probability of finding n nearby heavy particles is *decreased* with respect to the self-similar prediction. This makes sense, given that diffusive motions are recurrent for $d \leq 2$. Heavy particles which get close to each other meet often, strongly enhancing the probability of aggregation. This produces strong anti-correlation between particles which in turn causes the breakdown of self-similarity reflected by Eq.(4). These results may also be of interest in turbulence where the origin and quantification of multifractality remains an open problem of considerable interest.

References

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Contact Information: Colm Connaughton – CNLS & T13, MS-B213, Los Alamos National Laboratory, Los Alamos, NM 87545, Phone: (505) 667-7075, E-mail: connaughtonc@gmail.com.